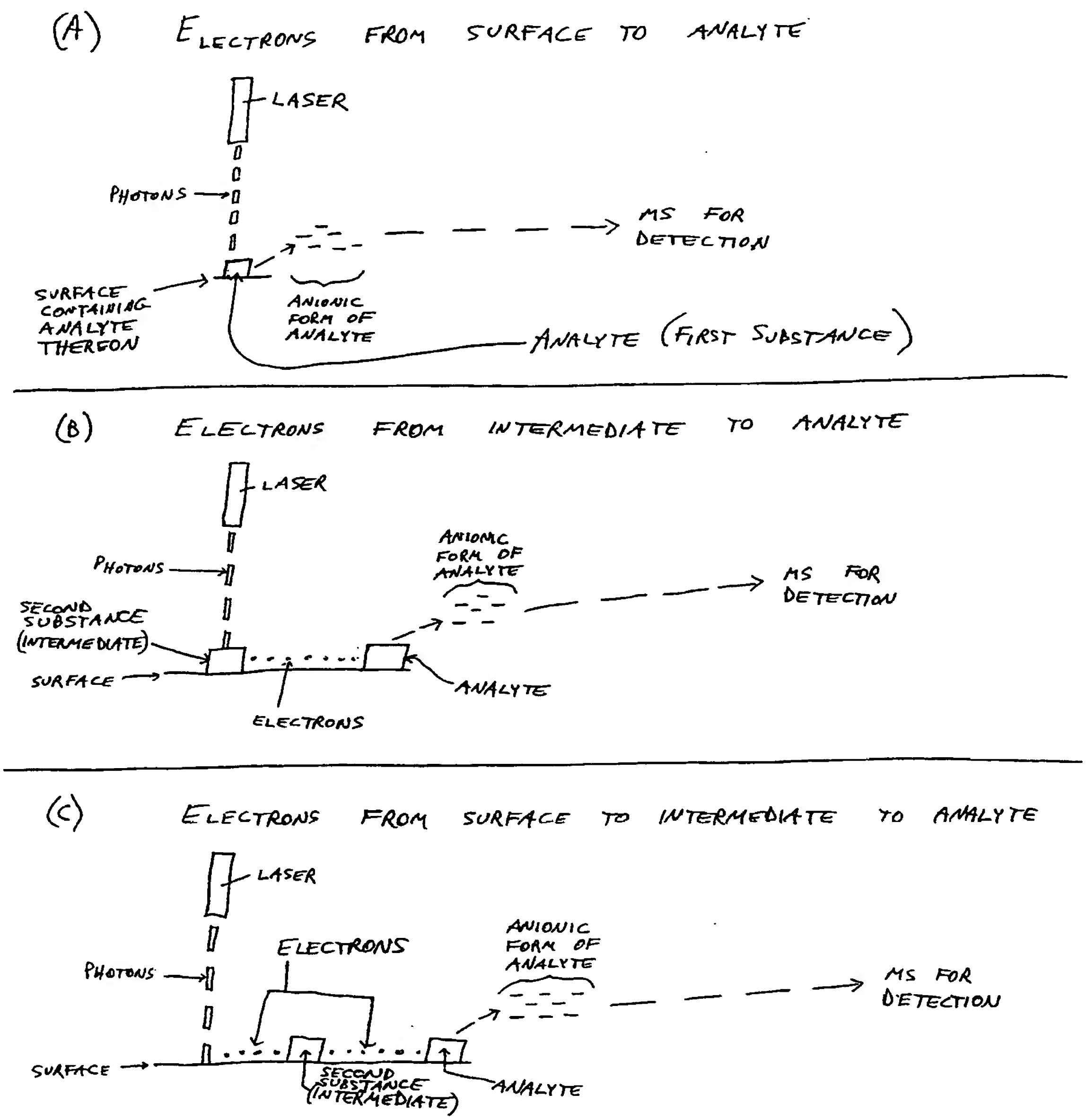
FIG. 1: LI-EC-MS


(A) ELECTRONS FROM SURFACE TO ANALYTE
LASER
PHOTONS
MS FOR DETECTION
SURFACE CONTAINING ANALYTE THEREON
ANIONIC FORM OF ANALYTE
ANALYTE (FIRST SUBSTANCE)
(B) ELECTRONS FROM INTERMEDIATE TO ANALYTE
LASER
PHOTONS
ANIONIC FORM OF ANALYTE
MS FOR DETECTION
SECOND SUBSTANCE (INTERMEDIATE)
SURFACE
ANALYTE
ELECTRONS
(C) ELECTRONS FROM SURFACE TO INTERMEDIATE TO ANALYTE
LASER
PHOTONS
ELECTRONS
ANIONIC FORM OF ANALYTE
MS FOR DETECTION
SURFACE
SECOND SUBSTANCE (INTERMEDIATE)
ANALYTE

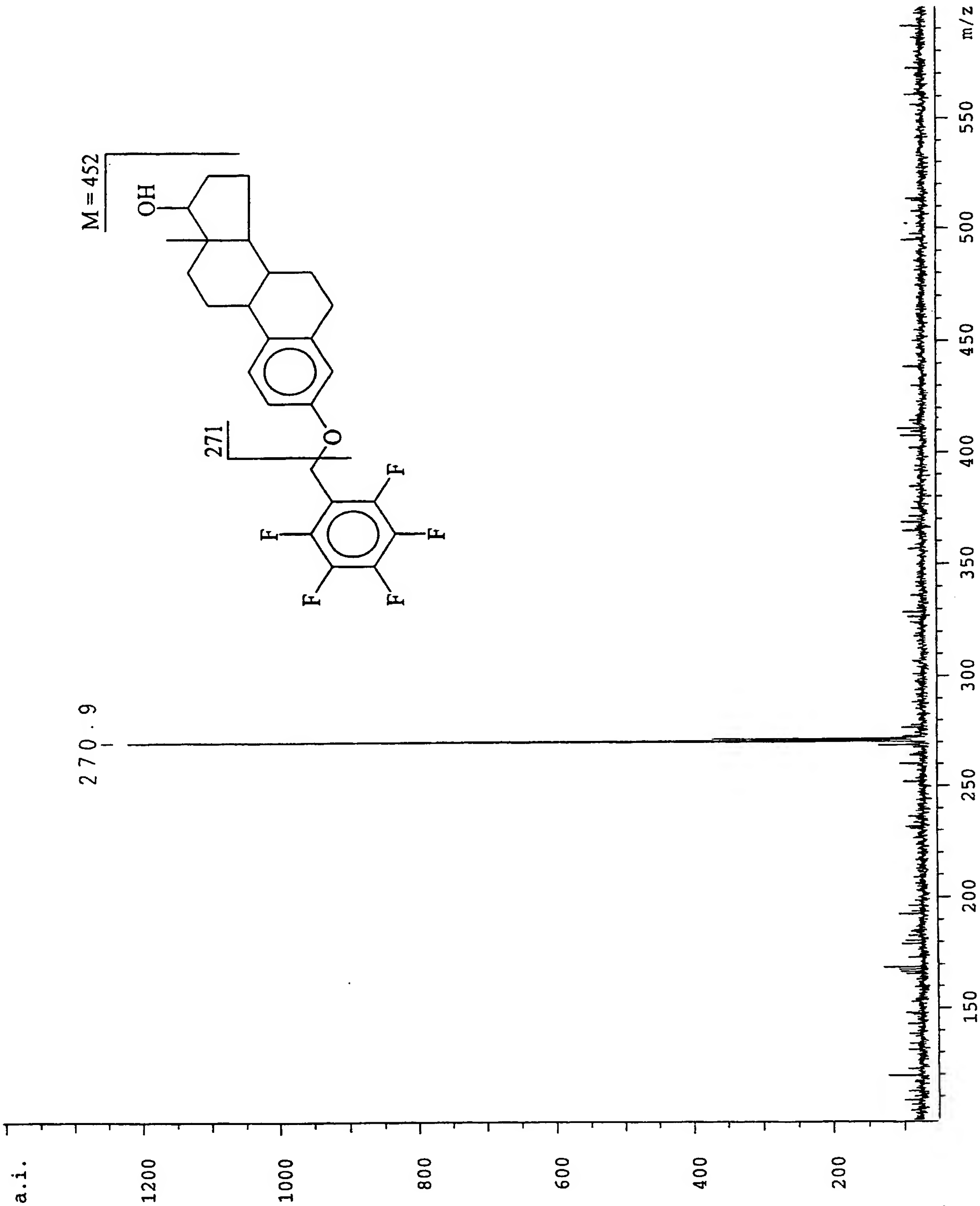
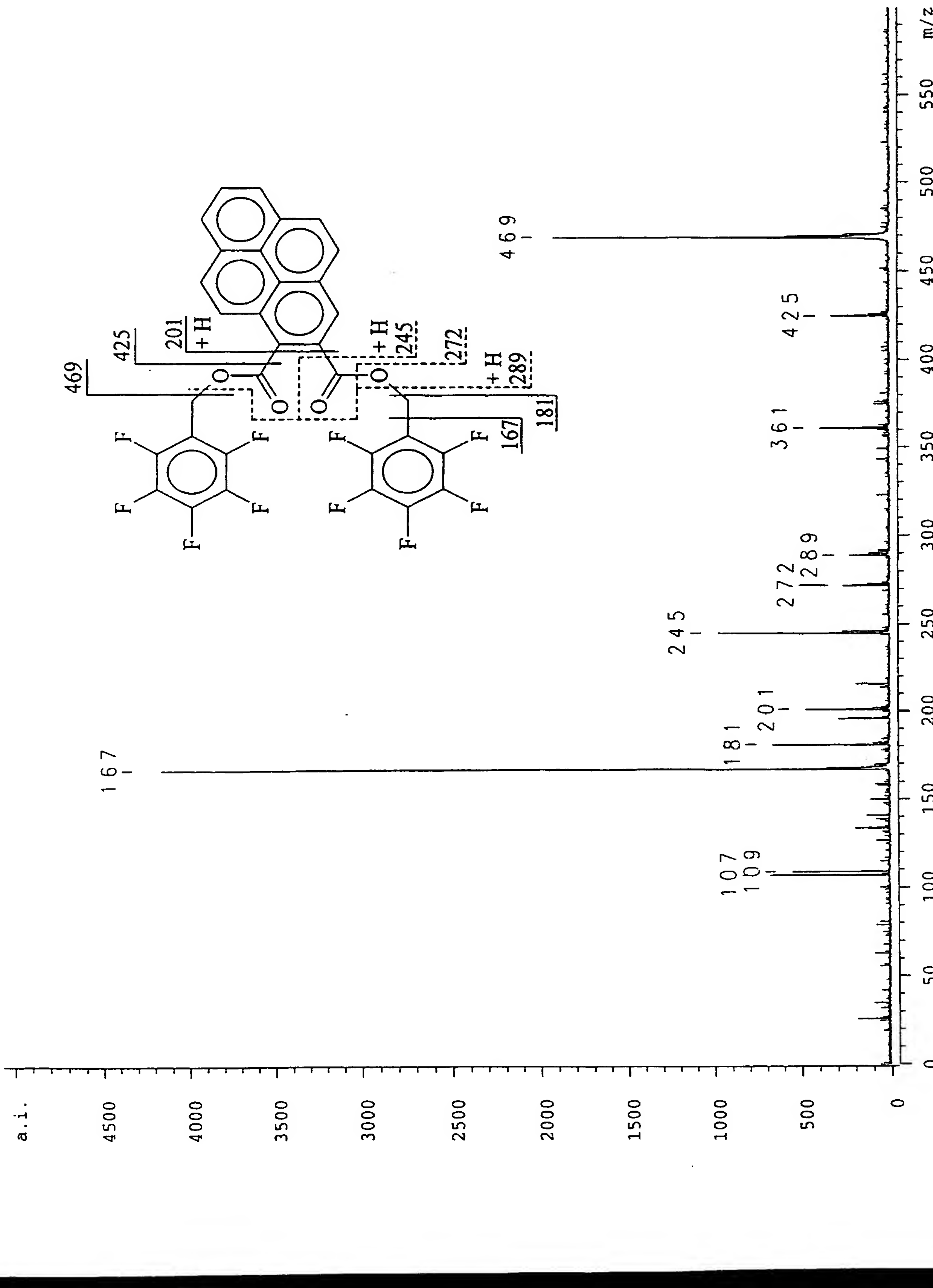

M = 452
OH
271
O
F
F
F
F
F
270.9
a.i.
1200
1000
800
600
400
200
150
200
250
300
350
400
450
500
550
m/z

Fig. 2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3500
3000
2500
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1500
1000
500
0
m/z
0
50
100
150
200
250
300
350
400
450
500
550
167
107
109
181
201
245
272
289
361
425
469
469
425
201
+H
+H
245
272
+H
289
181
167
F
O

Fig. 3

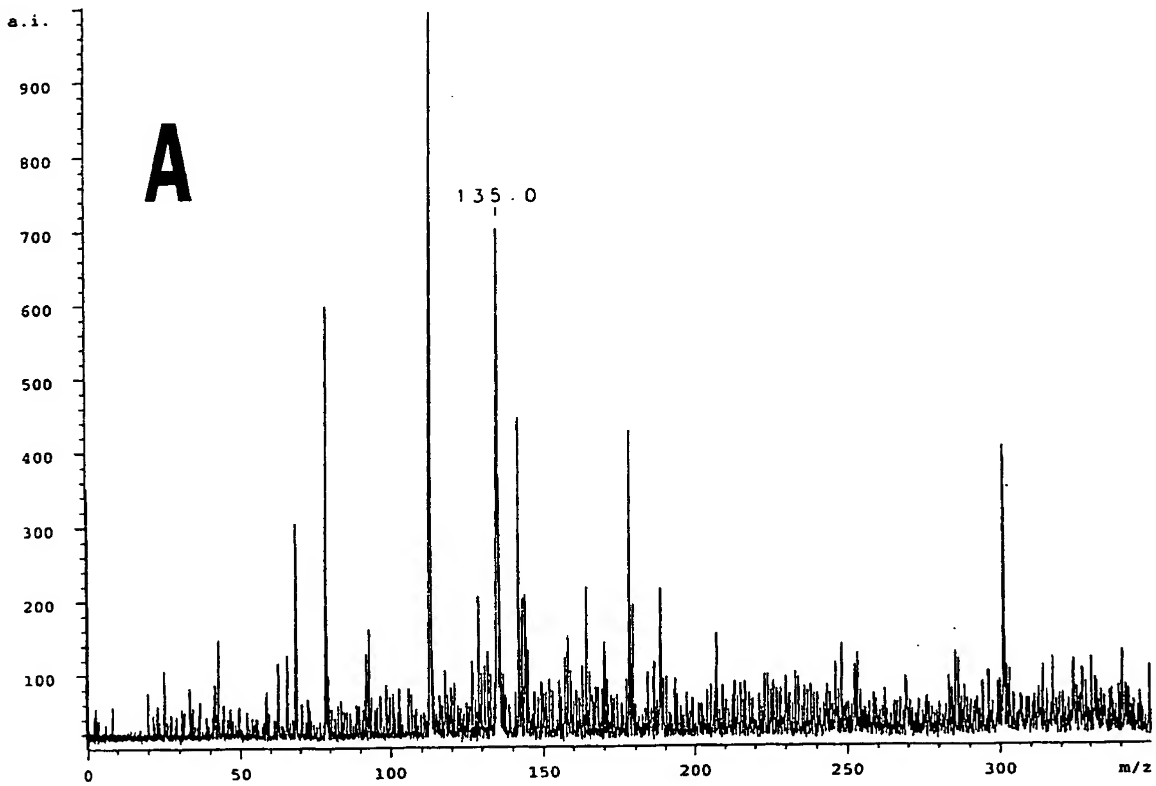
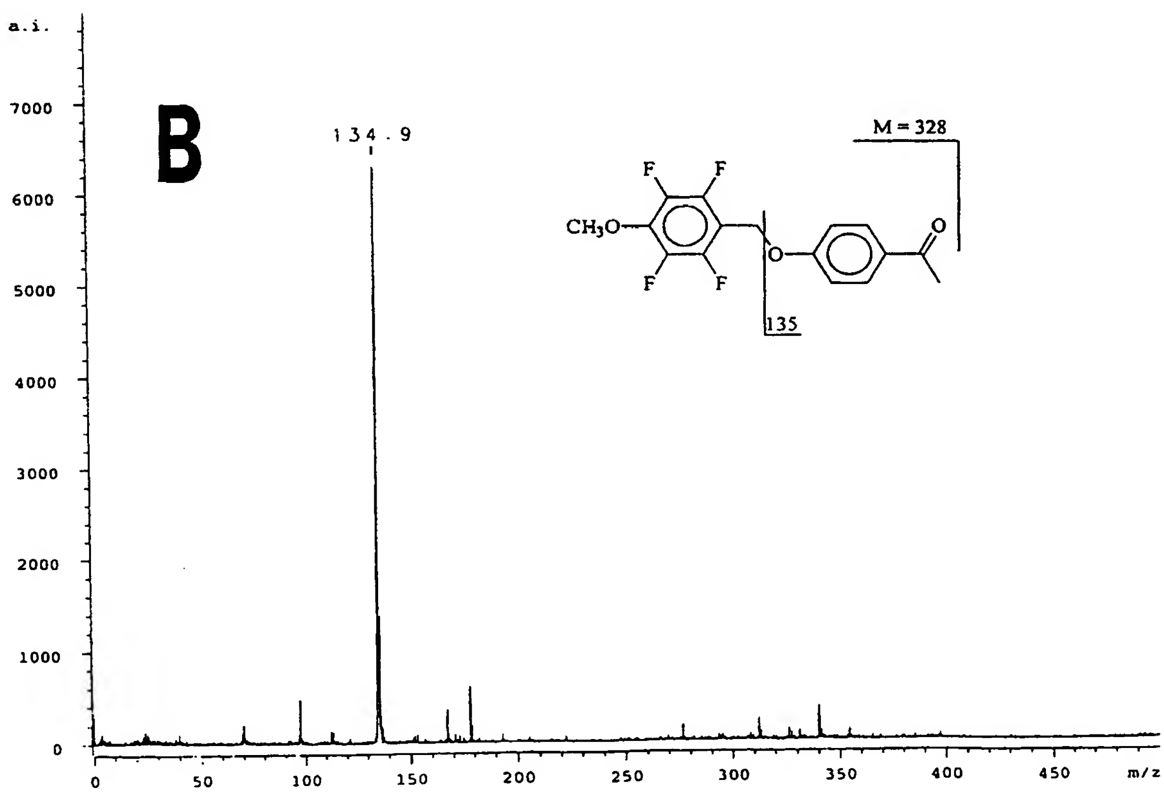

a.i.
900
800
700
600
500
400
300
200
100
A
135.0
0
50
100
150
200
250
300
m/z

Fig. 4a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5000
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1000
0
B
134.9
M = 328
F
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F
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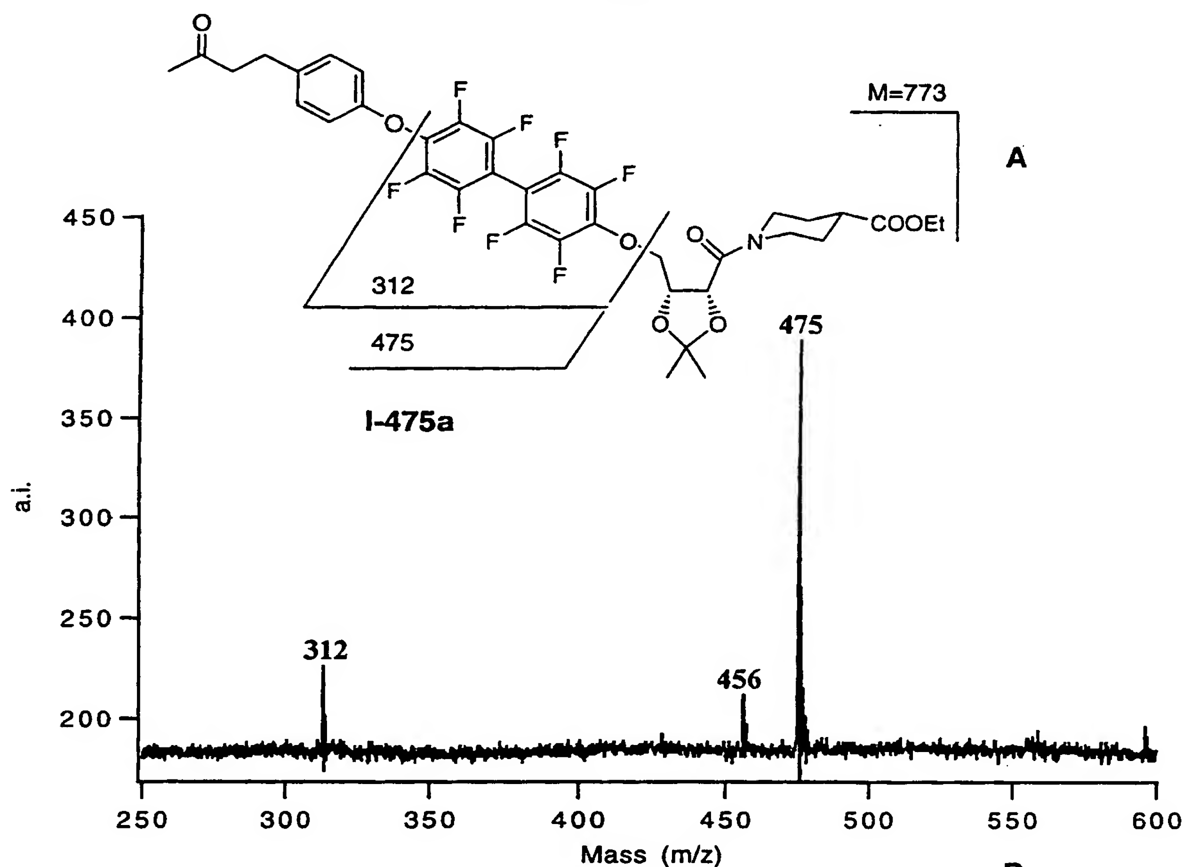
CH3O
O
O
135
0
50
100
150
200
250
300
350
400
450
m/z

Fig. 4b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I-475a
COOEt
450
400
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250
200
a.i.
312
456
475
250
300
350
400
450
500
550
600
Mass (m/z)

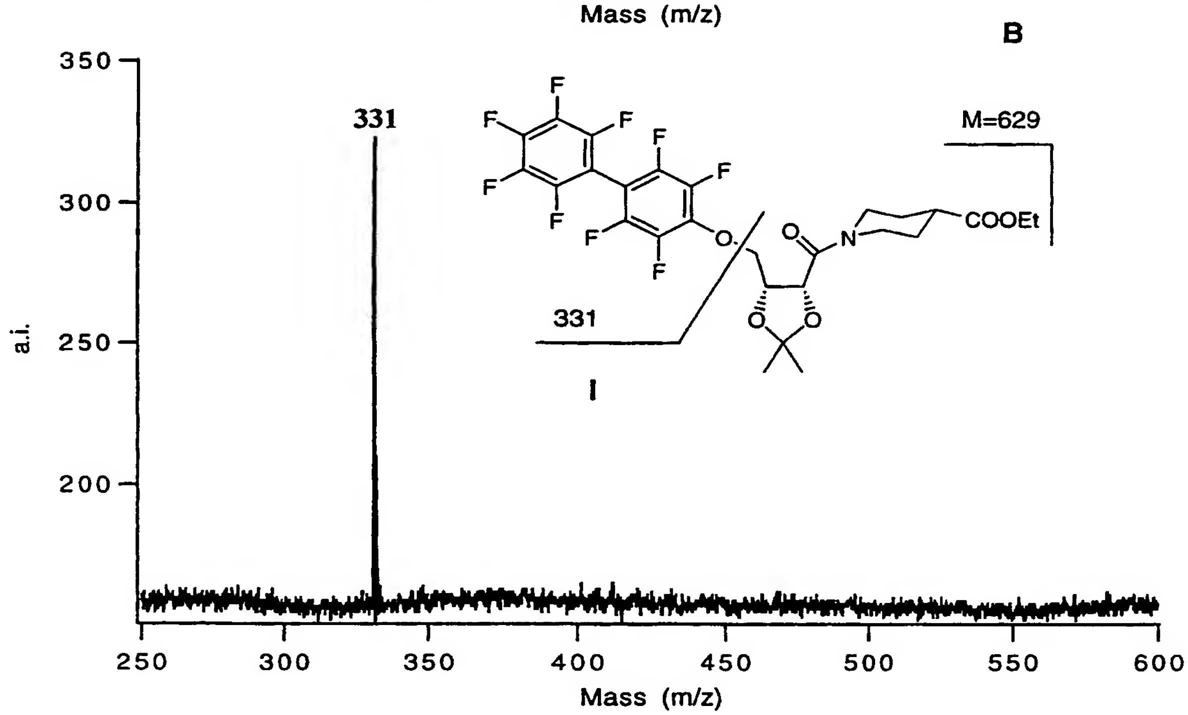
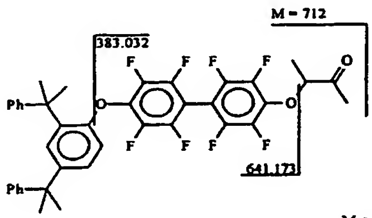
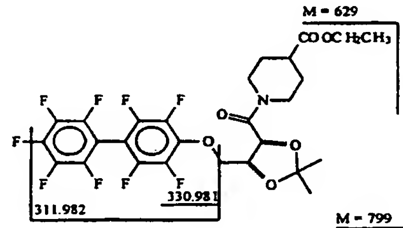

B
M=629
331
331
I
COOEt
350
300
250
200
a.i.
250
300
350
400
450
500
550
600
Mass (m/z)

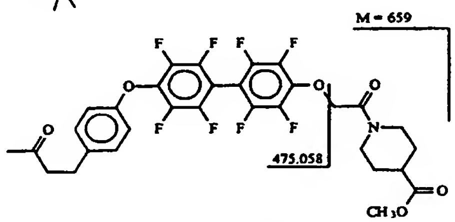
Fig. 5



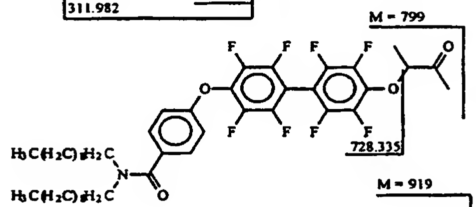
III-641a



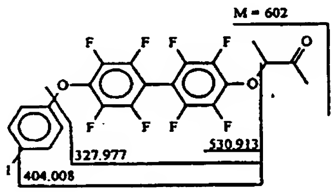
I-331a



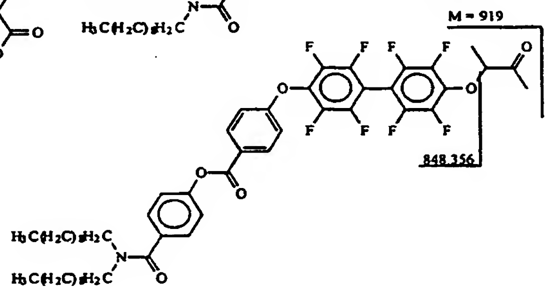
II-475a



III-728a



III-531a



III-848a

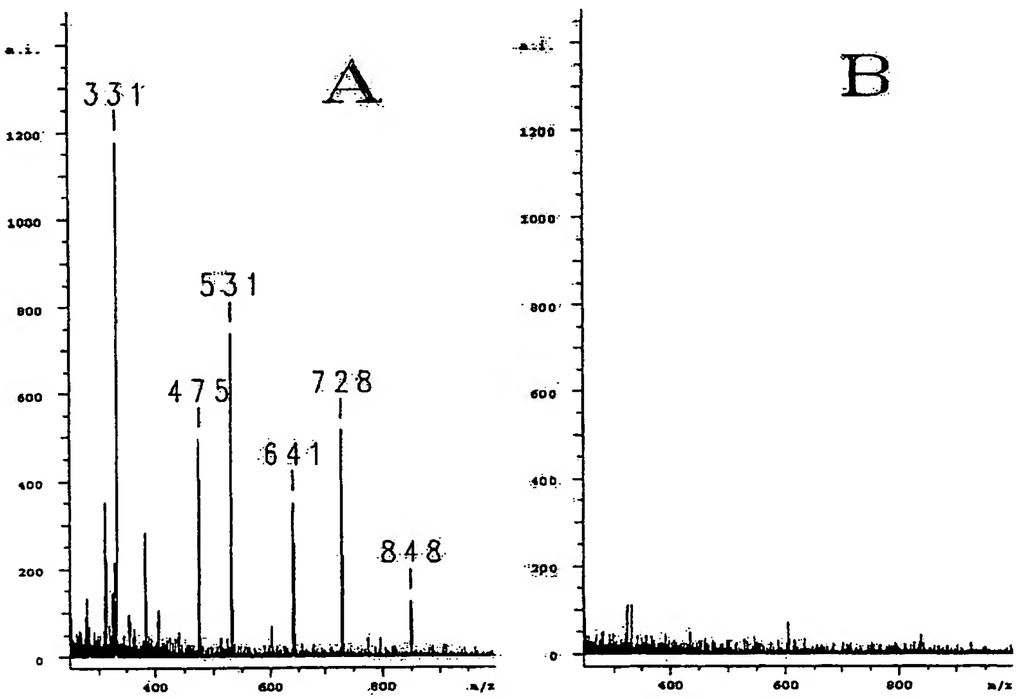


Fig. 6

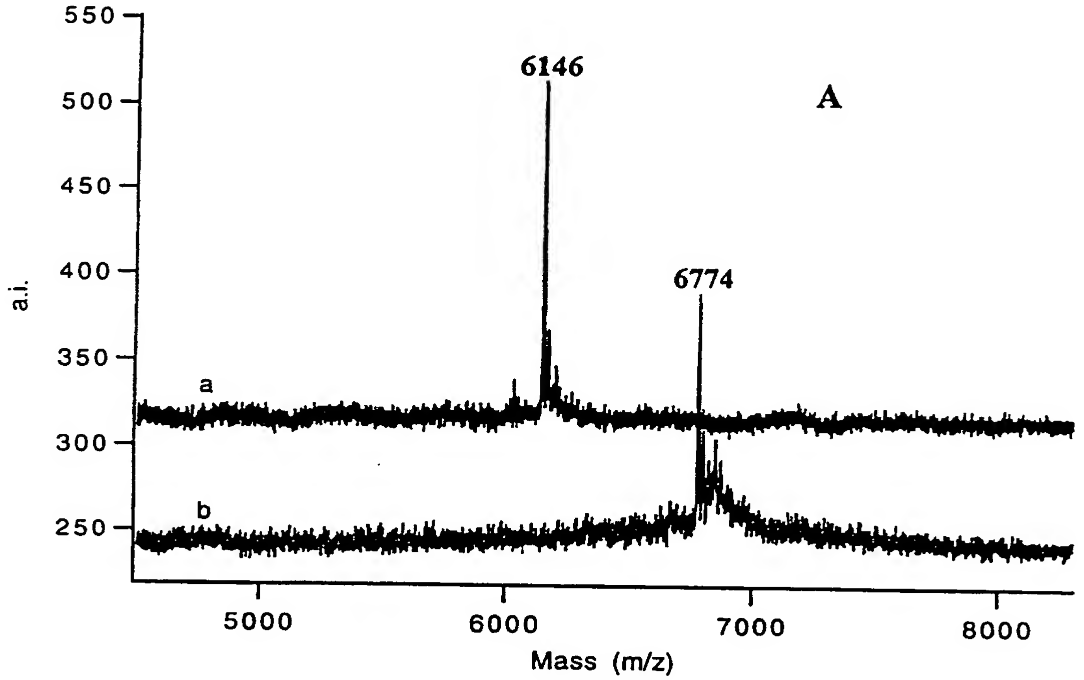

6146
A
6774
a
b
a.i.
550
500
450
400
350
300
250
5000
6000
7000
8000
Mass (m/z)

Fig. 7a

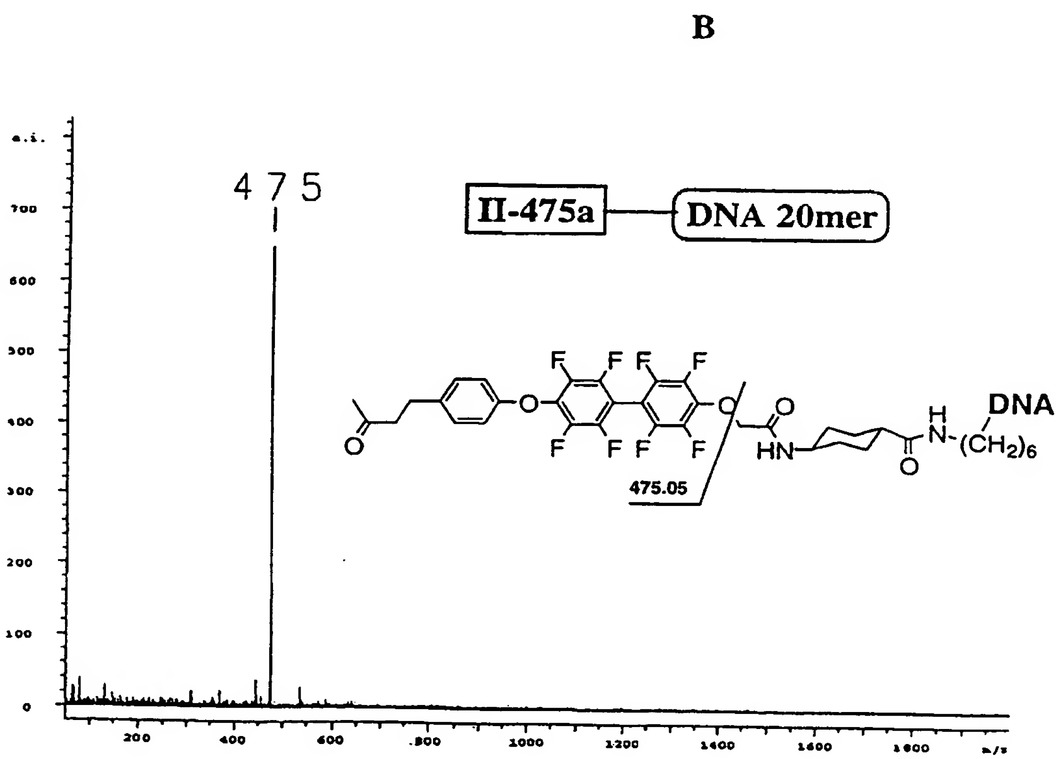
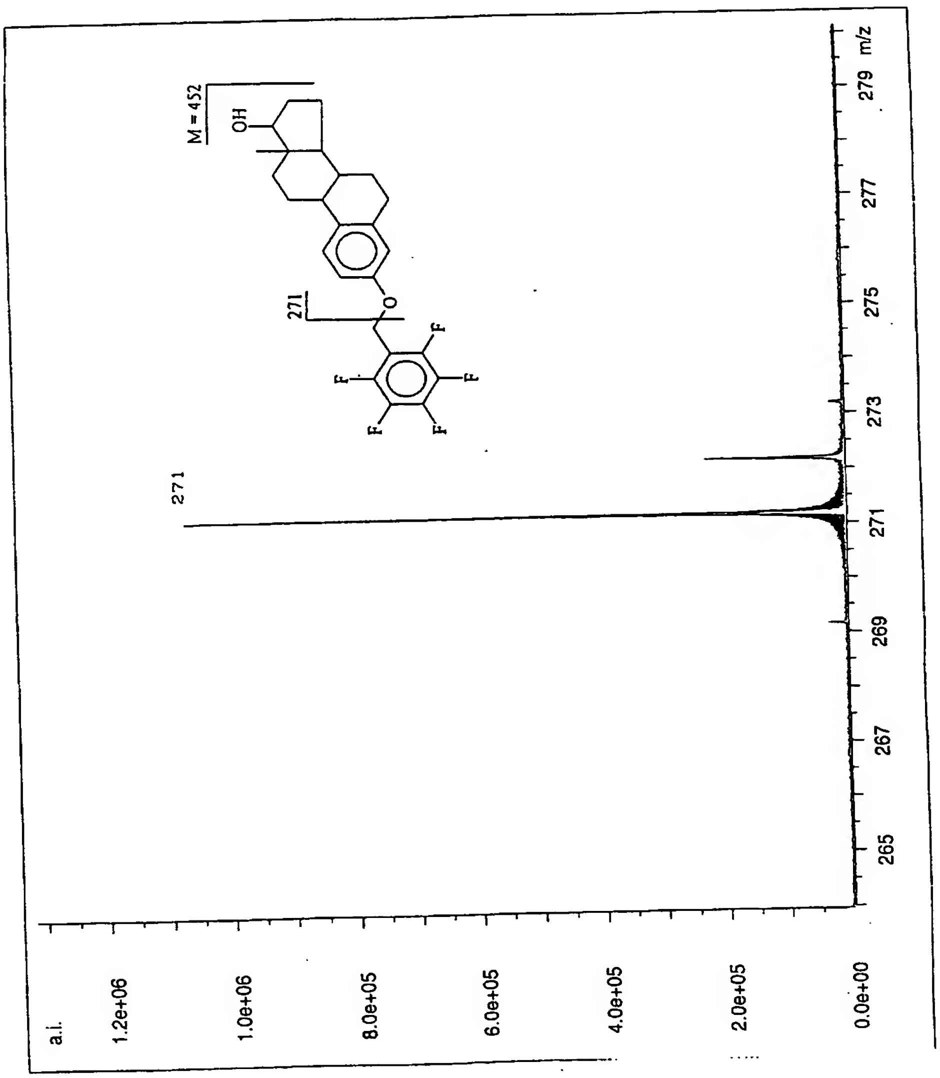

B
475
II-475a
DNA 20mer
475.05
DNA

Fig. 7b


a.i.
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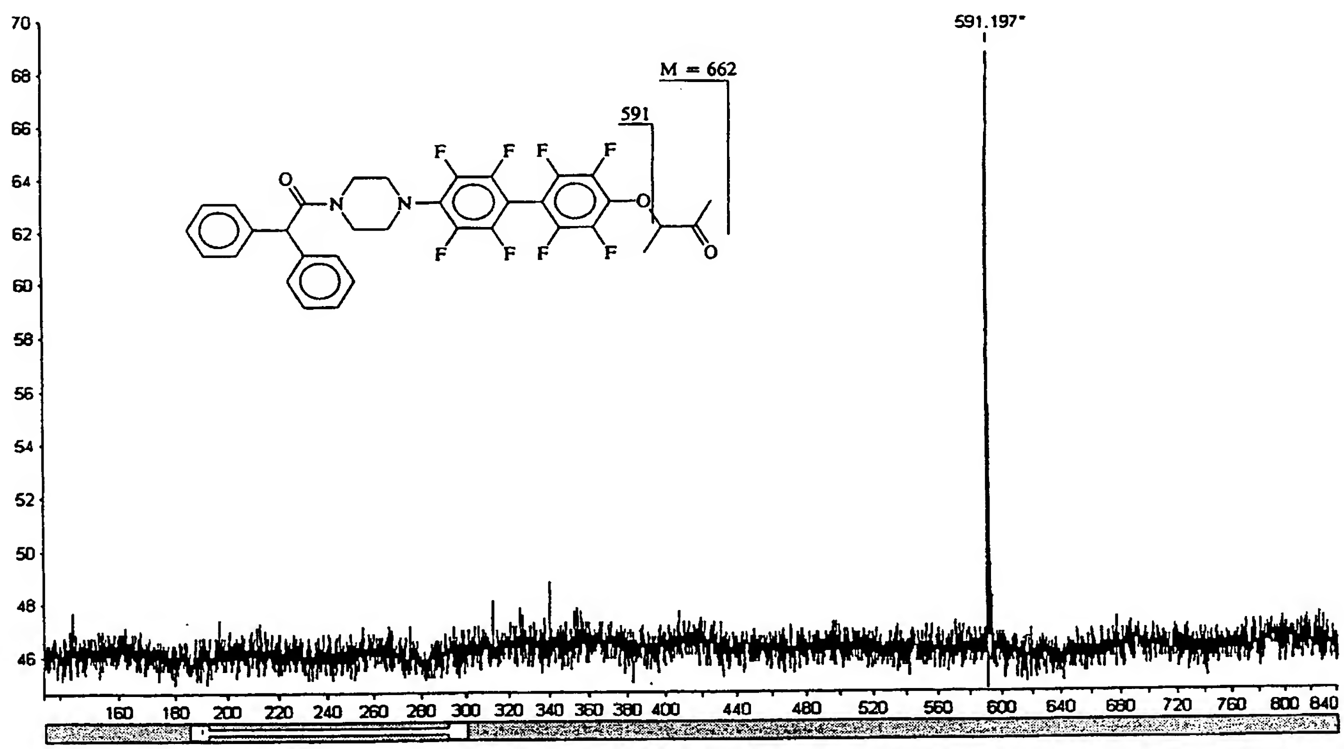
1.0e+06
8.0e+05
6.0e+05
4.0e+05
2.0e+05
0.0e+00
265
267
269
271
273
275
277
279
m/z
271
M = 452
271
OH
O
F

Fig. 8


591.197
M = 662
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F
F
F
F
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F
O
N
N
O
O
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68
66
64
62
60
58
56
54
52
50
48
46
160
180
200
220
240
260
280
300
320
340
360
380
400
440
480
520
560
600
640
680
720
760
800
840

Fig. 9

10/009042

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(71) Applicant *(for all designated States except US)*: NORTHEASTERN UNIVERSITY [US/US]; 360 Huntington Avenue, Boston, MA 02115 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: WANG, Poguang [CN/US]; 320 Salem Street #11, Medford, MA 02155 (US). ZHANG, Xin [CN/US]; 7 Rice Street #1, Brookline, MA 02445 (US). GIESE, Roger, W. [US/US]; 56 Oakland Avenue, Quincy, MA 02170 (US).

(74) Agents: HEINE, Holliday, C. et al.; Weingarten, Schurgin, Gagnebin & Hayes LLP, Ten Post Office Square, Boston, MA 02109 (US).

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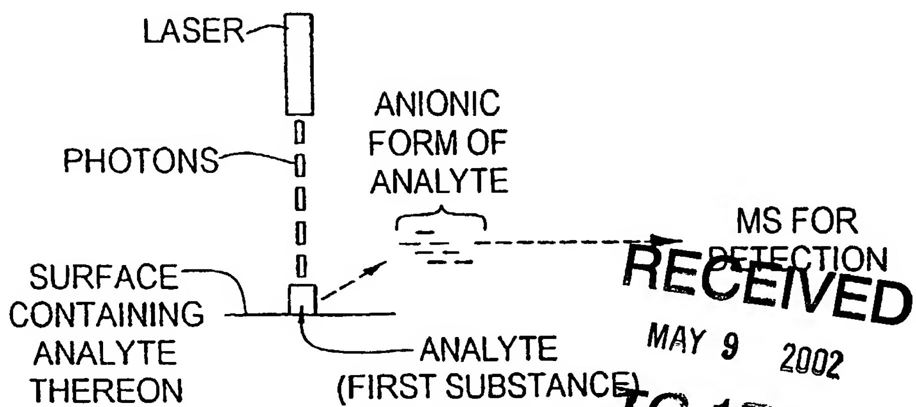

ELECTRONS FROM SURFACE TO ANALYTE

(57) Abstract: A method for increasing the performance and usefulness of laser induced electron capture mass spectrometry (LI-EC-MS). Light (photons) from a light source (laser), is used to activate an electron of a surface, preferably a metal surface, where the light energy is below the work function of the surface. The electron is transferred to an analyte on the surface, forming an anionic product from the analyte. The anionic product can simultaneously undergo desorption for detection in a mass spectrometer. Alternatively, the analyte (first substance) can receive an electron from an intermediate compound having a low ionization potential which is deposited with the analyte. This gives a sharpener or more intense signal from an analyte than prior forms of LI-EC-MS, but utilizes ordinary MS equipment. Further, the procedure even enables detection of species, such as nucleic acids labeled with polyfluoro-containing groups, that previously were beyond the reach of LI-EC-MS techniques.

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